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METHOD OF MANUFACTURING HYDROGELS

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ABSTRACT OF THE DISCLOSURE

Strong, elastic hydrogels are made by copolymerizing acrylonitrile or methacrylonitrile or mixtures thereof with co-monomers having hydrophilic side-groups, such as acrylamide, methacrylamide, acrylic acid, methacrylic acid and vinyl pyrrolidone or with mixtures of such co-monomers. The copolymerization is carried out in presence of free radicals and in an inorganic solvent which does not undergo any substantial chain transfer such as concentrated aqueous zinc chloride solution or nitric acid.

BACKGROUND OF THE INVENTION

According to my now abandoned U.S. patent application Ser. No. 43,926, filed June 6, 1970 and re-filed as 319,309 (Dec. 29, 1972) it is possible to prepare very strong hydrogels by free-radical polymerization of acrylonitrile or methacrylonitrile or mixtures thereof in acidic solvents which do not undergo chain transfer, followed by partial hydrolysis of the polymer so formed by dissolution or swelling thereof in the acidic solvents. In accordance with these teachings up to about 15 percent by weight of concentration of monomer can be used to provide the polymers which are soluble even in absence of chain transfer agents. At higher monomer concentrations, however, insoluble, more or less cross-linked hydrogels are obtained. The cross-linking is due mainly to chain transfer onto the monomer. Accordingly, the partial hydrolysis step causes some difficulty due to the cross-linking, especially when the monomer concentration is increased and it can be controlled only by the addition of chain transfer agents which reduce the chain length and are, therefore, not always advantageous.

OBJECT OF THE INVENTION

It is, therefore, a primary object of this invention to overcome such disadvantages by omitting the partial hydrolysis step. Other objects and advantages of the invention will be apparent from the following description thereof.

SUMMARY OF THE INVENTION

It has been found now that the partial hydrolysis, which causes such difficulties, particularly in case of large or thick articles, may be omitted, when acrylonitrile or methacrylonitrile are polymerized, that is, copolymerized with hydrophilic co-monomers in inorganic solvents which do not undergo substantially any chain transfer.

DESCRIPTION OF PREFERRED EMBODIMENTS

Among suitable hydrophilic monomers are acrylamide, methacrylamide, acrylic acid, methacrylic acid and the like. Exemplary of suitable inorganic solvents which undergo substantially no chain transfer there may be used preferably concentrated aqueous solutions of salts of the Hoffmeister series, such as zinc chloride, calcium rhodanide or lithium bromide, as well as concentrated nitric acid.

The cross-linking, as well as the hydrophilicity may be controlled more accurately and within very broad limits, depending on the kind of the co-monomer used. If, for

instance, a higher degree of branching or cross-linking is desired, at relatively low monomer concentrations, then acrylamide or acrylic acid are suitable as co-monomers. On the other hand, methacryl amide or methacrylic acid are capable of reducing the degree of cross-linking considerably, depending on their concentration. Thus, in such a case the monomer concentration can be considerably increased without obtaining too tightly cross-linked hydrogels. This is very important since, as mentioned above, the only other means for decreasing the degree of cross-linking, that is, the addition of chain transfer agents, reduces the chain length which is not always advantageous.

The omission of the partial hydrolysis step is also advantageous since the whole process of preparing the hydrogel is thereby considerably accelerated. The solvent may be removed just after the polymerization is finished and the swelling capacity is quite uniform on the surface, as well as in the interior of the casting, even in the case of large blocks. It is also further advantageous in that long cross-links, consisting entirely of carbon-to-carbon bonds and thus very resistant against hydrolytic or other agents, results. A usually employed cross-linking agent or compound may be also added in small amounts if desired, but the cross-links formed thereby are short and less resistant to chemical attack.

The copolymerization is advantageously carried out in the presence of free radical initiators and under external cooling so that the temperature of the polymerizing solution does not exceed 30° C. When using free radical redox initiators, the copolymerization can be carried out at external temperatures as low as between 0° and —50° C.

Hydrogels according to the invention may be used as a wide variety of end products, such as sorbents, dialysis materials, in surgical prostheses for replacing tissues and organs, carriers of biologically active substance such as drugs or pesticides, and hydrophilic coatings and the like. Soluble hydrogels according to the invention which contain amidic side-groups can be cross-linked with compounds having a functionality greater than one such as formaldehyde, dimethylol urea, hexamethylene tetramine, epoxides or poly-isocyanates and those containing carboxylic side-groups may be cross-linked by cations of polyvalent metals, such as chromium, aluminium and ferric cations. The same cross-linking agents may be used also to make sparingly cross-linked, highly swellable hydrogels which are less hydrophilic and stronger.

Cross-linked hydrogels of the invention possess excellent mechanical and physico-chemical properties such as tensile strength, elasticity and permeability for low-molecular solutes. Their chemical stability in neutral and weakly acidic media is good. They are optically isotropic, since they do not contain frequent long sequences of units of the same kind and have thus, little tendency to form crystalline regions.

In order to avoid bubbles and discoloration, it is preferable to remove the polymerization heat by external cooling, preferably maintaining the outer temperature below zero centigrade. Another means for suppressing small bubbles is to carry out the polymerization under increased pressure, by using the pressure of an inert gas in a closed mold. Increased pressure can be also obtained using a weight on a piston to compress the polymerizing mixture in the mold.

Th hydrogels of the invention are very suitable e.g. for manufacturing soft contact lenses. As mentioned before, since they are well compatible with living tissues and mucuous membranes, causing no irritation or inflammatory reactions, they may be advantageously used for making prostheses for tubular or other organs. Coatings made from soluble hydrogels may be subsequently cross-